1. Measuring Oleic Acid
   a. Experience with lab equipment, chemicals, lab procedure.
   b. Proof we can make measurements on the Nano-scale.
2. Putting the Nano-scale into perspective with macro-size objects.
   a. Give the student an idea what it means to work with Nano-sized particles, and a brief exercise relating to size scale.
3. Particle in a box
   a. See quantum effects of Nano-sized particles.
   b. Understand data taken from spectrometer, and making the connection between quantum dots and a “particle in a box”.

Nanotechnology Laboratory #1
Size and Scale

Utah Valley University

V1.1
Nanotechnology Laboratory #1

Size and Scale

Name________________________________________

Nanotechnology 1010 Laboratory #1

Size and Scale

Prelab Questions

Carefully read the laboratory and answer the following questions before coming to class. Once you have read the entire lab write-up and answered the questions correctly you may begin the experiment.

1. How many milliliters (ml) are there in 6.3 cubic centimeters (cm³)?

2. What equation gives the relationship between the cross-sectional area (A), the volume (V) and the length (L) of a cylinder?

3. If the area of a monolater of BB’s is 23.6 cm² and the total volume of the BB’s is 35.4 ml, what is the approximate diameter of a single BB?

4. What is the shape of an oleic acid molecule, according to the lab write-up?
5. If the diameter of a human hair is 0.00624 cm and the diameter of a typical atom is $2.40 \times 10^{-8}$ cm, how many atoms laid end-to-end would it take to make a length equal to the hair diameter?

6. If you wanted to make a dilute solution of oleic acid in alcohol containing 0.5% acid, how much acid should I add to a volume of alcohol equal to 20 ml?

7. How many Angstroms ($\text{Å}$) is one centimeter (cm)?

Introduction

Atoms are incredibly small. You are composed of about $5 \times 10^{27}$ atoms, an incomprehensibly large number. You might think that it would be impossible to measure the dimensions of an atom or molecule using simple lab equipment but it isn’t! In this lab you will exploit a property of oleic acid molecules that will make it possible for you to measure the length of the molecule.

Precautions and Safety Considerations

The methyl alcohol you will be using in this lab is a poison and must not be ingested. It is flammable so it must be kept away from all ignition sources. As with all chemicals, the oleic acid and alcohol should be contained and not spilled on skin or clothing. Protect your eyes with goggles and your hands with gloves. OLEIC ACID WILL STAIN certain types of clothing.

In part of the lab you will spread chalk dust on the surface of the water. Do not breath in the chalk dust. Be careful not to spill the oleic acid, the oleic acid and water mixture, or the BB’s on the floor since it will become extremely slippery and potentially dangerous. If and spills occur, immediately clean them up with paper towels and discard the used towels in the wastebasket.

The pipettes used to measure the oleic acid have a small piece of cotton at the top of the glass tube. The purpose of the cotton is to keep liquid from escaping from the end of the glass tube. If you suck too much oleic acid into the pipette do that some reaches the cotton, the pipette will become useless and will have to be thrown away!
Technique

Since molecules are so small, we will not be able to measure them in any conventional way with a ruler. Instead we will have to use a technique that will work even though we cannot see or touch an individual molecule. If the molecules can be arranged in a monolayer (an ordered layer only one molecule thick with no empty space between adjacent molecules), and if the surface area of the layer and the total volume of the molecules making up the layer can be measured, then the thickness of the monolayer can be calculated from the formula:

\[
\text{Monolayer Thickness} = \frac{\text{Volume}}{\text{Surface Area}}.
\]

This formula can be derived from the equation describing the relationship between volume, surface area, and length.

Oleic acid molecules have the property that they will form a monolayer if placed on the surface of water! So the experiment involves measuring out a very small volume of oleic acid molecules, then gently dropping the molecules onto the surface of a pool of still water and measuring the area off the monolayer surface. From other experiments it is known that the shape of an oleic acid molecule is approximately cylindrical, and the length of the cylinder is much larger than the diameter. It turns out that the molecules in the monolayer arrange themselves so that the cylinders are all standing straight up. Thus, our measurement of the monolayer thickness is really a measurement of the length of the oleic acid molecule.

(Note: Oleic acid acts in some ways like oil. To prevent oil from our hands from interfering with the experiment, try to avoid touching with ungloved hands anything that will eventually come in contact with the oleic acid: the insides of graduated cylinders, beakers, trays etc.)

To make the lab possible we need to have a monolayer surface area that is small enough to fit comfortably on a laboratory table. The volume of molecules contained in one drop from a dropper is about two hundred times larger than needed. However, if the oleic acid is diluted in methyl alcohol, when the oleic acid/alcohol mixture hits the water, the alcohol will dissolve into the water leaving the oleic acid behind on the surface. Thus, a mixture that is about 200 parts alcohol to 1 part oleic acid will be needed.
The surface area of the monolayer can be measure by sprinkling a fine powder uniformly on the surface of the water before dropping the drop of oleic acid/alcohol mixture on the water. As the oleic acid spreads out into a monolayer, it will push the fine chalk dust outwards keeping it from penetrating the monolayer. So the monolayer can be detected as the part of the water that is free from chalk dust.

Materials and Equipment

- Safety goggles
- rubber gloves
-.50 ml of Oleic acid
- chalk or lycopodium powder
-100 ml of methyl alcohol
- calibrated pipette with rubber bulb
-100 ml graduated cylinder
-10 ml graduated cylinder
- dropper
- sandpaper(if using chalk)
- Large Tray
-1 liter Beaker
- Water
- Ruler

Measuring the Size of Oleic Acid Molecules

Since we are using chemicals, we need to put on safety goggles and gloves. Be sure to adjust the straps of the goggles so that they are comfortable an neither too tight note too loose.
Procedure

Prepare the dilute solution of Oleic acid in methyl alcohol

We want to dilute the Oleic acid to a 0.5%, i.e. 5 parts in 1000 or 5:1000. To do this we will add .50 ml of Oleic acid to 100 ml of methyl alcohol. The .50 ml of acid will be dispensed from a calibrated pipette, and the 100 ml of alcohol will be measured in a 100 ml graduated cylinder.

   a) Fill a 100 ml graduated cylinder with methyl alcohol. You measure volumes with a graduated cylinder by letting the bottom of the center of the liquid surface reach the graduation line.

   b) Carefully draw some Oleic acid into the cylinder of the pipette using the rubber bulb. Remember that the pipetter will be ruined if you suck oleic acid into the cotton at the upper end of the glass tube. Be careful to hold the bottom of the pipetter always below the surface of the acid so that no bubbles are sucked into the pipette. Make sure you know what each line designation on the pipette represents. Although you will only release 0.5 ml of acid into the alcohol, draw about 0.6 to 0.7 ml.

   c) Using the graduations on the pipette, carefully release 0.5 ml of oleic acid into the graduation cylinder filled with the methyl alcohol. Release the remaining oleic acid in the pipette back into the bottle.

   d) Stir the mixture with a glass stirring rod many times to mix the chemicals.

Now you have a great quantity (100.5 ml) of a dilute oleic acid/alcohol mixture. You will only use a small amount of this in the experiment.

Volume of Oleic Acid Mixture in One Dropper

We will select a small volume of the oleic acid mixture by using a dropper. We will need to determine the volume of a drop of mixture released by the dropper. To do this, we see how many drops it takes to make exactly 1 ml of mixture, and then we will divide 1ml by the number of drops to determine the volume of one drop.
a) Take the 10 ml graduated cylinder and carefully count how many drops from the dropper it takes to fill it to 1 ml. You may want to practice making a few drops before you start to fill the cylinder. Remember, you measure volumes with a graduated cylinder by letting the bottom of the center of the liquid surface reach the graduation line. Record the number of drops here:

-Number of drops to make 1 ml:_____________________________

b) Divide 1ml by the number of drops to determine the volume of 1 drop, and record your result here:

- Volume of one drop of oleic acid/alcohol mixture: _____________ml.

c) The volume of oleic acid in the mixture is only 0.50% of the mixture volume. So multiply the volume of one drop by 0.005 to obtain the volume of oleic acid inside one drop, and record your result here:

- Volume of oleic acid in 1 drop of oleic acid/alcohol solution: _____________ml.

Surface area of an oleic acid monolayer

Now you are ready to prepare the water layer and spread fine chalk dust over it. Before you being, however, it is important to realize that the chalk particles are typically hundreds or thousands of ties larger than the thickness of the oleic acid monolayer. If your body were the size of the oleic acid molecules, the chalk particles would appear to be mountains floating on the liquid surface. You need to take care to make small chalk particles, to not put too many on the liquid surface, and not to clump many particles together. Most students who obtain poor results for this lab make the mistake of using too much chalk dust on the surface of the water.

Follow the procedure below, and when you are finished you will be ready to make the monolayer of oleic acid and measure its surface area.

1) Your tray needs to be very clean in order to get good results. Before doing anything, thoroughly clean the tray with alcohol and paper towels. After cleaning, be very careful to keep the tray clean. Don’t put anything in it other than what the instructions say, and don’t touch the inside surface of the tray with ungloved hands.

2) Take the large 1 liter beaker and get enough water from the faucet to fill the tray to about ½ inch (1 to 1.3 cm) depth. Make sure the tray is level.
3) Hold the mall chalk and sandpaper about a foot above the water and gently sand toff some of the halk so as to lightly cover the water surface. The goal is to end up with the water surface looking like it is covered in a very fine layer of very fine dust. Use only enough chalk so that you can just see the chalk on the water surface. Too much chalk will prevent the oleic acid from spreading into a monolayer. If the chalk clumps together on the water surface, you have used too much chalk. If you can clearly see individual chalk particles on the surface, the chalk particles are too large. Also, be careful not to breathe the chalk dust.

4) You can now drop a single drop of oleic acid/ alcohol mixture into the center of the tray. Remember to release the drop at a height of about 1 cm about the liquid surface.

5) After the ‘circle’ of oleic acid stops shrinking, measure its diameter at about 5 points space uniformly around the edge, and record your values here:

   Diameter of monolayer of oleic acid ( cm )

   __________  __________  __________  __________  __________  __________

6) Put another drop of the mixture into the center of the oleic acid film. You have roughly doubled the volume of the oleic acid film. Since the thickness should be fixed at one molecule thickness, the area should have also doubled. A circle with twice the area has about 1.4 times the diameter of the smaller circle.

   Has the area of your circle about doubled?____________________________

7) Average the 5 diameters measured in step 5 and record your result here, using 3 significant figures.

   Average diameter of the oleic acid monolayer:_________________cm

8) Calculate the area of the circle and record your result:

   Surface area of oleic acid monolayer:_________________cm$^2$. 
9) Using your volume of the oleic acid in your drop and the measured surface area of the monolayer, calculate the thickness of the oleic acid monolayer and record it here:

Thickness of the oleic acid monolayer: __________________________ cm.

The Angstrom Unit of Length

Although atoms don’t have well defined edges, we can talk about their sizes. For example, the size can be taken to be equal to the spacing between adjacent atoms in a crystal. The atoms of the various elements vary in size by about a factor of four. The size of the smallest atom, hydrogen, is about $1 \times 10^{-8}$ cm. The unit of length called the Angstrom is defined to be $1 \times 10^{-8}$ cm, and is the convenient length unit to use when dealing with atoms or molecules. It is named in honor of Anders Jons Angstrom (1814-1874), a Swedish physicist who made important contributions to the study of the wavelength of light emitted by various atoms.

1) Convert the length of the oleic acid monolayer from centimeters to Angstroms:

_________________________ Å.

Final Steps: Clean up!

1) Empty the water from your tray into the designated container or sink.
2) Dry the tray with a clean paper towel after removing any chalk dust that remains.
3) Rinse out the 100 ml and 10 ml graduated cylinders that contained the oleic acid/alcohol mixture.
4) Throw away your glass pipette and place the bulb from it and your dropper in the designated area.
5) Wipe your table with paper towels to clean up any water that may have spilled on the table.
Part Two: Putting it into Perspective!

The size of the Oleic acid molecule that you calculated above is difficult to imagine or even compare to macro-sized objects that we are used to seeing every day. To put things into perspective we are going to blow things up.
Let’s imagine we can scale up a thin human hair to the size of the Empire State Building. Our new scale will make a 17µm hair 443 meters tall! If we continue knowing this scale, then we can predict the size of other objects as well. Fill in the blanks below to see how big each object would be on an empire state building sized scale.

If a red blood cell is about 6 µm in diameter, it would become _______ 158 meters tall.

A small bacteria cell is about 0.5 µm in diameter, which puts it at _______ 13 meters tall on our blown-up scale.

A virus, which can be around 100nm in diameter, is how many times smaller than our bacteria? How tall on the buildings scale? 5 times smaller. This virus would stand 2.6 meters tall on our Empires State building.

This leads to the conclusion that 1 nanometer is going to be just ___________ 2.6mm off the ground!

How many one-nm objects would it take to span across our 17µm hair? 17000
Part Three: Particle in a Box

Theory

The particle in a box problem is hard to visualize. This is because there is not a good real world example of a particle in a box. However, there is one good example that can now be used: Quantum Dots. Inside small semiconductors that make up microprocessors and flash drives there are small semiconductor particles. These can contain one electron and one “hole” or absence of an electron. These are real world particles in a box because they can never get outside of the semiconductor and by observing the Quantum Dots the effects of changing the size of the box on the energy levels of the system can be observed.

As you remember, the particle in a box taught us that energy levels are quantized and inversely proportional to the square of the length of the box. That energy can be represented by:

\[ E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} \]  

(eq. 1)

The equation used to determine the energy of a quantum dots is extremely similar. The nature of a semiconductors forces us to account for not one energy term, but three. First, our energy equation needs to account for the mass of two particles, an electron\( (m_e) \) and a hole from the absence of an electron\( (m_h) \). The third term is the energy of the semiconductor bandgap \( (E_g) \):

\[ E_{\text{quantum dot}} = \frac{\pi^2 \hbar^2}{2m_eR^2} + \frac{\pi^2 \hbar^2}{2m_hR^2} + E_g \]  

(eq. 2)

Use the values given below for the mass of an electron, the hole, and the bandgap energy.

\[ E_g = 2.15 \times 10^{-19} \text{ J} \]
\[ m_e = 7.29 \times 10^{-32} \text{ kg} \]
\[ m_h = 5.47 \times 10^{-31} \text{ kg} \]
To understand where these terms come from a brief discussion of semiconductors is required. After all, quantum dots are just tiny semiconductors that take on some of the same special properties of atoms because they are so small.

**Semiconductors**

Semiconductors are materials which have a conductivity between conductors (generally metals) and insulators (such as most ceramics). They can made from pure elements like silicon or germanium, or compounds such as gallium arsenide or cadmium selenide. In a process called doping, small amounts of impurities are added to pure semiconductors which will both change its conductance and cause them to conduct electricity under some conditions but not others, making them a good medium for the control of electrical current. A change in the applied voltage or current, temperature, or the intensity of light can change the conductance of semiconductors, allowing electrons to flow.

When impurities are added to a pure substance like silicon, the conductance is generally increased. This is because there has been a change to the crystalline structure of the atoms. In our example below, Silicon has 4 valance electrons per atom and its 2-dimensional crystalline structure looks like this:

![Crystalline structure of silicon](image)

By doping the silicon semiconductor with an atom that has one extra valence electron we end up replacing a small percentage of the silicon atoms with the new atoms containing 5 valence electrons.
This extra electron is not held in place with the same forces as the ones paired in covalent bonds and is able to move about the crystalline structure more freely, causing an increase in the electric conductivity of the semiconductor. This is because once the extra electron starts moving about the lattice it leaves behind an empty, low energy quantum state, or “hole”, that wants to be occupied, causing a “flow” of electrons from the adjacent silicon atoms.

**Band Theory**

As stated above, a semiconductor is something that has a conductivity somewhere between a conductor and an insulator. Now that we know how a semiconductor’s conductance can be changed with doping, let’s look at what conductance is on the atomic level.

Atoms consist of a nucleus, and electrons that orbit around it. These orbits are in discrete shells. An atom such as sodium has two electrons in the inner shell, eight in the next shell and one its outermost shell. The outermost electron is in a shell that is referred to as the *valence band* or *valence shell*. This single electron is very loosely held and contributes to the reactivity of sodium, and with a potential difference this electron is free to move. Because of this, this band will also be referred to as the *conduction band*. 
The valence band and the conduction band are not always the same thing, however! Pictured below is a similar diagram, but of a chlorine atom. Notice that chlorine has 7 electrons in its valence band, but this time they are very tightly held and do not have enough energy to become conductors in their current position. To become conductors, they have to move to the conduction band that is in the next shell. Right now, there are no electrons in this conduction band. For an electron to get promoted to the conduction band it needs to cross a what is called the **forbidden gap**.

![Diagram](image)

We know that electrons have discrete energy levels. To move to the conduction band an electron will need a specific amount of energy. For insulators, this is actually a very large energy gap to overcome. Below is a good visualization of the relationship of the conduction and valance bands for insulators, conductors, and semiconductors.

![Diagram](image)

From the figure above, you can see that the valence and conduction bands of a conductor overlap, but the forbidden gap of an insulator is large enough that no electrons can reach the conduction bands. For a semiconductor, the forbidden gap can be small enough that just a
change in thermal energy can allow electrons to go from the valence band to the conduction band, allowing the material to conduct when a potential difference is applied.

**Quantum Dots**

The background information above is the basis for understanding how and what quantum dots are. As previously stated, quantum dots are semiconductors. They are also a real example of a particle in a box.

When an atom absorbs a discrete amount of energy, an electron gets promoted to an excited state, falls back down, then emits a photon. The wavelength, or color, is directly related to how much energy the electron gained. The amount of energy it takes to get promoted to an excited energy state is called **band gap energy**. This is exactly what is happening in semiconductors. The band gap for a semiconductor is the amount of energy required for an electron to go from the valence band to the conductance band. The nature of quantum dots allows them to behave in a manner similar to atoms and semiconductors. When you dope a semiconductor, you are changing the amount of energy required for an electron to cross a band gap. This is like forcing an atom to have only one discrete energy level so that it emits a photon of a very specific wavelength. For a quantum dot, changing the band gap is literally changing the size of this “Nano-sized” semiconductor. This relationship between the size of the quantum dot and the emission spectra is that we will explore in this laboratory experiment.

**Materials Needed:**

- Particle in a box experiment
- Flashlight
- Metal Stands
- OceanOptics Spectrometer and Fiber Optic Cable
- Ocean View Software
- Excel or Similar Spreadsheet program

**Procedure**

1. Plug in the Ocean optics fiber optic cable into the Red Tide spectrometer. Then plug in the red tide unit to the computer via the USB cable provided.

2. Open the OceanView/Spectra Suite software.

3. Click “Spectroscopy application wizards”.
4. Click the "Fluorescence" button

5. Click "Active acquisition".

6. Ocean view will then ask you to store data from the light that is coming in from the background. This includes the ceiling lights, and the flashlight we will use to illuminate the quantum dots. By doing this, the software will filter out the background light and give us data from only the quantum dots. Shine the flashlight into the optical cable from a few feet away to get a good reading on the graph. Make sure the intensity isn’t too high. Once you are satisfied with how your graph looks, click finish.

7. Now take time to toggle over the icons at the top of the graph so you can scale your data/graph to fill the viewing window.

8. Notice there are 2 tabs open. One for "view minus background " and one for "view". Compare the two to see why filtering out the background spectra helps us view the quantum dot spectra.

9. If you click on the graph near a peak you can see the wavelength displayed on the lower left-hand part of the graph.

10. A spreadsheet containing the data points from each graph can be found by using the "view result in table form" button near the top of your graph.

Now that you are familiar with the operation of the software we can collect some data.

11. Clamp your quantum dots upright, very gently, on a metal stand or any place that will give you easy access to the underside of the vials.

12. Position your fiber optic cable so that it also is on a metal stand and pointing at the quantum dot vials. You will need to be able to adjust the position of the cable to view all the vials throughout the experiment.

13. Using the provided flashlight, illuminate the underside of one of the vials so that the flashlight is perpendicular to the optical cable. Point the optical cable directly at the vial, getting it as close as possible. You should see the emission spectra on your computer.
14. Take a screen shot of the graph and copy/paste it into excel, **making sure to label it with the peak wavelength from that vial.**

15. The peak wavelength can be found from the spreadsheet data in the software. Copy and paste that data into Excel next to its corresponding graph screenshot.

16. Using equation 2 in the Theory section above, calculate the radius of the Quantum Dots for each vial and put it in your spreadsheet. Be sure your answer is in Nanometers.

17. Calculate the percent error between your measured wavelength and dot radius verses the actual values provided by your instructor for each vial. Place this data in your spreadsheet.

18. Plot the quantum dot radius verses the emitted wavelength for each vial, on a single graph in Excel. What relationship do you see?

19. What happens if the radius of the quantum dot gets very large(approaching infinity)?